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REMARKS

Claims 1-26 are pending in this application. At the outset, Applicants thank the Examiner for indicating that claim 26 would be allowable if rewritten in independent form including all of the limitations of the base claim and any intervening claims.

Upon entry of this Amendment, claim 1 has been amended to delete “olefin polymers” from the Markush group. Claims 2 and 14 have been cancelled in consideration of the amendment to claim 1.

Claim Rejections

Rejection Under 35 U.S.C. § 112, second paragraph

Response to Rejection of Claim 14 under 35 U.S.C. § 112, second paragraph as being indefinite.

By this amendment, claim 14 has been canceled. Applicants submit that this rejection is now moot. Reconsideration and withdrawal respectfully are requested.

Rejection Under 35 U.S.C. § 102/§ 103

A. **Response to Rejection of Claims 1-23 and 25 under 35 U.S.C. § 102(b) as being anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over Burton.**

In response to the rejection of claims 1-23 and 25 under 35 U.S.C. § 102(b) as being anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over US Patent No. 6,017,986 of Burton (“Burton”), Applicants respectfully submit that the reference does not teach all the elements of the amended claims and that that a *prima facie* case of obviousness has not been made out by the Examiner, and respectfully traverse the rejection.

Burton teaches a radiation-resistant polyolefin composition consisting essentially of a polyolefin and at least one aliphatic, unsaturated compound. In contrast, the presently claimed invention discloses a preparatory process and a composition of a non-olefin polymer with improved thermal stability. Therefore, the reference does not teach all the elements of the

presently claimed invention.

With respect to the rejection under § 103, in order to establish a *prima facie* case of obviousness based on a single reference, the Examiner must establish all three of the following essential criteria: (1) there must be a motivation in the cited prior art to modify the reference as suggested by the Examiner; (2) the cited reference must teach or suggest each of the claimed elements; and (3) the cited reference must provide a basis for a reasonable expectation for success. The motivation to modify and the reasonable expectation for success must come from the cited prior art and not the Applicants' specification. Further, it is not enough that a reference can be modified absent a suggestion in the cited prior art to undertake such modification.

As discussed above, Burton does not teach or suggest all the elements of the presently claimed invention since Burton only discloses the use of an aliphatic compound in an olefin polymer to prepare a radiation-resistant polyolefin composition, not the non-olefin polymer of the presently claimed invention. Burton further states that it is well known in the art that polyolefin articles tend to become brittle upon exposure to high energy radiation (column 1, lines 19-22). This brittleness is due to a polyolefin oxidation process after radiation in the presence of oxygen. (RADIATION-RESSISTANT POLYMERS, Encyclopedia of Polymer Science and Engineering, 2nd ed., volume 13, page 693, herein attached.) In contrast, the presently claimed invention concerns the thermal stability of the polymers. The polymer can thermally depolymerize under high temperature, but the existence of oxygen is not required since it is not an oxidation process. Olefin polymers are usually much more resistant to thermal depolymerization as compared to the polymers claimed in the present invention, such as polystyrene, polymethyl methacrylate or grafted polyolefin with side chain of acrylic acid esters. For example, Table 3 of review article, "DEPOLYMERIZATION" shows that after heat treatment at a thermal depolymerization temperature of 300-500 degC, polyethylene and polypropylene have depolymerized by only 0.03 and 0.2-2 wt%, respectively, whereas polymethyl methacrylate, and polystyrene lost its polymer by 92-100 and 42 wt%, respectively. (Encyclopedia of Polymer Science and Engineering, 2nd ed., volume 4, page 733, herein attached).

Since Burton deals with the oxidation process in the presence of oxygen, while the present invention relates to depolymerization at high temperature, they solve entirely different

technical problems and therefore, there is no suggestion or motivation to be found with the cited reference to use an unsaturated aliphatic compound in non-olefin polymers in order to improve the thermal stability. Further, there is no reasonable expectation of success in modifying the reference as suggested by the Examiner to arrive at the presently claimed invention, since the polymers claimed in the present invention can degrade via the thermal depolymerization process, whereas the polyolefin claimed in Burton does not. Therefore, since none of the elements of a *prima facie* case of obviousness has been set forth, reconsideration and withdrawal of the rejection respectively is requested.

B. Response to Rejection of Claims 1-8, 10-20 and 22-24 under 35 U.S.C. § 103(a) as being unpatentable over Syed in view of Burton.

In response to the rejection of claims 1-8, 10-20 and 22-24 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 6,046,273 of Syed (“Syed”) in view of U.S. Patent No. 6,017,986 of Burton (“Burton”), Applicants respectfully submit that a *prima facie* case of obviousness has not been made out by the Examiner and respectfully traverse the rejection.

First, the Examiner has indicated that Burton taught the use of oils for polyolefins in order to improve radiation and heat resistance in the abstract. Applicants respectfully disagree. As discussed above, Burton discloses a radiation-resistant polyolefin composition in which at least one aliphatic, unsaturated compound is used. The technical issue solved by Burton is to increase the radiation resistance of polyolefins by reducing the rate of oxidation induced by radiation. In contrast, Syed teaches a process for improving the thermal stability of alpha-substituted acrylate graft copolymers by copolymerizing 1-3 C alkyl-substituted acrylic acid with an ester of a 1-3 C alkyl-substituted acrylic acid. (column 2, lines 35-41). Syed indicates that since “poly(methyl methacrylate) tends to lose weight by depolymerization”, various levels of methacrylic acid makes the copolymer more stable at a given temperature than the graft copolymer made with 100% MMA or MMA/MeAc. (column 7, line 65 to column 8, line 18.) Therefore, the thermal stability achieved by Syed is by incorporation of acrylic acid into the grafted polymers by copolymerization. Although Syed does disclose that other additives, such as oil can also be present in the acrylate-grafted copolymers (column 6, line 41), there is no suggestion that the use of oil can increase the thermal stability of the polymer.

In addition, Burton is directed to the radiation resistance of polyolefins relating to an oxidation process, whereas Syed is directed to the thermal stability of acrylic polymers by using a copolymerization process. Therefore, there is no motivation to use the unsaturated compound disclosed Burton in the non-olefin polymer system of Syed to improve the thermal stability. Applicants respectfully submit that there is no *prima facie* case has been made out.

However, even if a *prima facie* case of obviousness has been established, Applicants submit that unexpected results have been achieved when combining the unsaturated aliphatic compound with the non-olefin polymers. Figures 2 and 3 of the specification of the present invention show that the residue MMA concentration increases with the decrease of iodine numbers (page 21, Table 4). As described in the specification, the “degree of retardation of polymer degradation was found to depend on the degree of unsaturation of the unsaturated aliphatic compound and its concentration in the formulation.” It further stated that “minimum amount of unsaturation (iodine number of 10) is required.” (page 11, lines 7-11). Since Syed only teaches the addition of oil in a polymer system, it would have been unexpected for one skilled in the art to discover that the unsaturated aliphatic compound can increase the thermal stability of the polymer but saturated oil does not. Reconsideration and withdrawal of the rejection respectfully is requested.

C. Response to Rejection of Claims 1-10 and 12-22 under 35 U.S.C. § 102(b) as being anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over Pillar.

In response to the rejection of claims 1-10 and 12-22 under 35 U.S.C. § 102(b) as being anticipated by or, in the alternative, under 35 U.S.C. § 103(a) as obvious over US Patent No. 4,032,481 by Pillar, Applicants respectfully submit that the reference does not teach all the elements of the amended claims and that a *prima facie* case of obviousness has not been made out by the Examiner, and respectfully traverse the rejection.

Pillar teaches the use of epoxidized soybean oil in a polystyrene composition (column 3, lines 54-55). Since the epoxidized soybean oil prepared by the reaction of natural soybean oil with hydrogen peroxide (column 3, lines 41-42) contains an epoxy group in place of its double bond, it is no longer unsaturated, and therefore Pillar does not teach all the elements of the presently claimed invention, such that, “about 0.1% to about 5%, based on the weight of the

polymer, of at least one aliphatic compound having at least one site of unsaturation, the compound having a molecular weight of at least 200 and an iodine number of at least 10.” (page 30, 12-15.)

With respect to the obviousness rejection, Applicants submit that Pillar only teaches the use of expoxidized soybean oil. Since such expoxidized soybean oil is not a compound having at least one site of unsaturation, it is different than the compound claimed in the present invention. and there is no suggestion or motivation to use an unsaturated aliphatic compound to increase the polymer thermal stability to be found in the cited reference. Reconsideration and withdrawal of the rejection respectfully requested.

D. Response to Rejection of Claims 1-23 under 35 U.S.C. § 103(a) as being obvious over Nakamura et al.

In response to the rejection of claims 1-23 under 35 U.S.C. § 103(a) as being obvious over US Patent No. 6,107,377 of Nakamura et al (“Nakamura”), Applicants respectfully submit that a *prima facie* case of obviousness has not been made out by the Examiner and respectfully traverse the rejection.

As noted by the Examiner, Nakamura only teach the addition of polybutadiene into the polypropylene resin (column 4, line 12), whereas the presently claimed invention discloses the addition of polybutadiene to non-olefin polymers. Since Nakamura do not teach or suggest the use of polybutadiene to improve thermal stability of polyolefins and in fact polyolefins are usually not sensitive to thermal degradation caused by depolymerization as discussed above, there is no suggestion or motivation for a person skilled in the art to add polybutadiene to the non-olefin polymers claimed in the present invention to improve their thermal stability.

Reconsideration and withdrawal of the Rejection respectfully is requested.

Applicants submit that the application stands in condition for allowance. Should the Examiner have questions or comments regarding this application or this amendment, Applicant’s attorney would welcome the opportunity to discuss the case with the Examiner.

The Commissioner is hereby authorized to charge U.S. PTO Deposit Account 08-2336 in the amount of all fees required for consideration of this Amendment.

This is intended to be a complete response to the Office Action mailed September 22, 2003.

Respectfully submitted,

ABUZAR SYED ET AL.

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February 19, 2004
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VOLUME 13

Poly(phenylene Ether)
to
Radical Polymerization

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lower dose rate. At a sufficiently low dose rate, oxygen diffusion effects would disappear, resulting in homogeneous oxidation throughout. Because temperature affects the oxygen diffusion rate and also possibly other steps in the oxidation mechanism, the oxygen penetration depth depends on temperature as well as dose rate. Thus, polymeric samples irradiated in the presence of oxygen can undergo different changes in the interior and exterior regions. The relative size of these regions depends on sample thickness, oxygen pressure in the surrounding atmosphere, dose rate, and temperature (73).

At sufficiently high dose rates, oxidation takes place only at the immediate surface. In such cases, most of the material undergoes degradation under effectively anaerobic conditions. The overall property changes are often similar to those for samples irradiated under inert atmospheres, and the conclusions and figures presented previously may approximately apply. However, this is not always the case. For instance, for hard glassy materials, an oxidatively degraded surface layer may be much more susceptible to crack formation under stress. Such cracks, once formed, may propagate readily through the bulk of the sample, and properties such as flexural strength may reflect a significant surface effect (74). For situations that approach homogeneous oxidation, homogeneous-oxidationlike degradation behaviors are often approximated. When both oxidized and unoxidized (or slightly oxidized) regions comprise a significant fraction of the material, the material properties may be a complex sum of the individual properties of the two regions. Frequently, macroscopic properties of heterogeneously degraded samples are between those obtained with materials oxidized homogeneously and materials degraded under inert atmosphere. For a series of different samples with progressively deeper oxidation, properties often range progressively from near those of samples degraded in an inert atmosphere to near those of homogeneously oxidized samples (73).

Heterogeneous oxidation appears frequently. Many applications involve material thicknesses and dose rates that result in heterogeneous oxidation. In addition, for applications that may involve dose rates so low as to give homogeneous oxidation, accelerated radiation-aging experiments, performed to predict degradation behaviors, which employ short time periods and elevated dose rates frequently give rise to heterogeneous oxidation. As a rule of thumb on oxygen-diffusion effects, it can be noted (73) that many elastomers and flexible plastics exhibit strongly heterogeneous oxidation when samples ca 1-mm thick are irradiated in air over the dose-rate range of 10^2 – 10^4 Gy/h (10^4 – 10^6 rad/h). For hard, glassy materials with lower permeation rates, oxygen diffusion effects would be expected at a lower dose-rate range.

Methods for Studying Radiation-induced Oxidative Degradation. The methods described above for studying radiation degradation in an inert atmosphere also apply to degradation in the presence of air. Swelling experiments and other techniques, which reveal molecular weight or cross-link density changes, have been widely used, as have mechanical property measurements (tensile tests, etc). Using esr and uv spectroscopy, the conversion of carbon-centered radicals to peroxy radicals (eq. 11) on admission of oxygen to preirradiated materials can be readily studied (75,76). Among spectroscopic techniques, it is particularly useful for monitoring polymer oxidation (77) because carbonyl bands (~ 1725 cm^{-1}) stand out strongly. Thermally induced chemiluminescence is another use-

ful technique for studying oxidation kinetics (78). Gaseous analyses, eg, gas chromatography or mass spectroscopy, are frequently employed to monitor radiation oxidation. Loss of oxygen from the atmosphere surrounding the samples in an enclosed container is often measured, as well as the production of gaseous oxidation products (79-81) (especially CO_2 and CO).

Special techniques have been employed for examining heterogeneously oxidized samples. Detailed profiles of heterogeneous degradation can be obtained by means of microhardness measurements. By plotting the depth of indentation of a tiny, weighted probe as a function of position across the cross-sectional surface of an irradiated degraded sample, a profile of changes in relative hardness (or modulus) is obtained (73,82,83). Figure 12 shows a hardness profile for a Viton sample irradiated in air. Near the edges, where extensive oxidation took place, the material underwent scission and became softer. In the interior, where degradation took place in the absence of oxygen, the material underwent cross-linking and became harder.

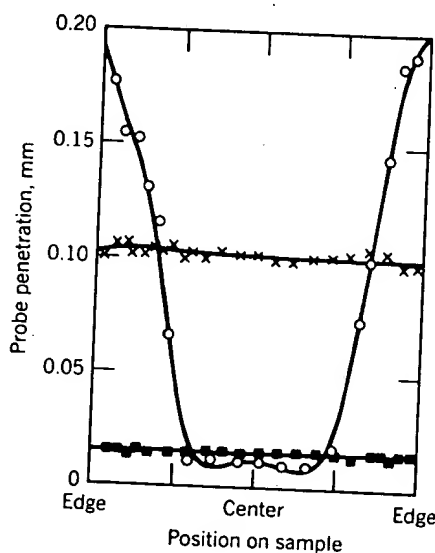


Fig. 12. Hardness profiles for γ -irradiated Viton fluorelastomer samples, 1.9-mm thick (1 Gy = 100 rad). \times , unirradiated material; \bigcirc , 1.8×10^3 Gy/h in air to 1.9×10^6 Gy; \blacksquare , 9×10^3 Gy/h in vacuum to a dose of 1.9×10^6 Gy (73).

Other profiling techniques require sectioning of degraded samples into successive slices, often using a vibratome. A given property, measured for each slice, is plotted as a function of the position of origination of the slices, from edge to interior. Properties that have been measured by this method include density (84), which is very sensitive to oxidation and can be readily measured with a density gradient column; solution viscosity (74,85,86), which can be related directly to molecular weight changes; gel fraction after solvent extraction (87), ir spectrum (88); and chemiluminescence (89). Oxidation profiles vary, depending on the particular material and the experimental conditions. In some cases, they may take the form of sharp transitions between oxidized and nonoxidized regions. In other

cases, they may have parabolic shapes that correspond to lower oxidation at the center than at the edges. Rapid, qualitative identification of the occurrence of heterogeneous oxidation can often be achieved by polishing the cross-sectional surface of a degraded sample using standard metallographic techniques. Areas of the sample with very different extents of oxidation have different hardness, and take on different lusters on polishing; differences in reflectivity are directly apparent on optical examination (73). The heterogeneous oxidation in a sample of cross-linked polyethylene irradiated in air (90) is shown in Figure 13.

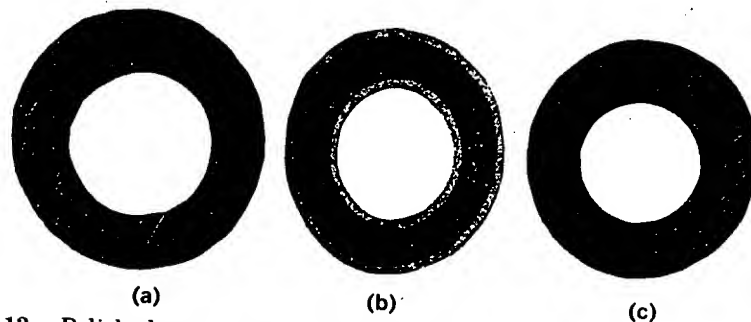


Fig. 13. Polished cross-sections of cross-linked polyethylene cable insulation material, illustrating heterogeneous oxidation at high dose rate in air (1 Gy = 100 rad). (a) Unirradiated material; (b) 8.9×10^3 Gy/h to 1.2×10^6 Gy in air; (c) 1.1×10^4 Gy/h to 1.1×10^6 Gy under vacuum. Samples were stripped off the copper conductor, and irradiated as hollow tubes; wall thickness = 0.75 mm (90).

Dose-rate Effects. When polymeric materials are irradiated in the presence of oxygen, the rate of degradation and the nature of degradation can be strongly influenced by the dose rate. Lower dose rates often increase oxidation and chain-scission yields, and result in more extensive material degradation per equivalent absorbed dose. Dose-rate effects are one of several mechanistically related, time-dependent phenomena that occur in radiation oxidation; others include temperature dependence and postirradiation effects. Dose-rate effects arise whenever one or more steps in the oxidation chemistry become rate-limiting on a time scale comparable to the experimental time period of interest; most commonly they are due to oxygen diffusion, peroxide breakdown, and radical migration.

Dose-rate effects can have dramatic practical consequences. When irradiated pipes constructed of low density polyethylene were pressurized to 4 N/mm² (580 psi) and the time to rupture was measured, the following observation was made. For pipes irradiated at high dose rate (10^6 Gy/h or 10^8 rad/h), rupture time was increased from the initial (unirradiated) value of 100 h up to 10^4 h at doses of 2×10^5 Gy (2×10^7 rad) or higher. For pipes irradiated at low dose rate (4 Gy/h or 400 rad/h), rupture times dropped to less than 1 min at doses above 7×10^4 Gy (7×10^6 rad) (91). For power cables exposed to long-term irradiation at low dose rate (0.25 Gy/h or 25 rad/h) in the containment room of a nuclear reactor, the polyethylene insulation was completely embrittled after a dose of 2.5×10^4 Gy (2.5×10^6 rad). In short-term, high dose-rate laboratory experiments (10^4

Gy/h or 10^6 rad/h), there was no detectable change in mechanical properties of this same material (within experimental error) after the same dose; embrittlement of the material required $>10^6$ Gy (10^8 rad) (92). When a Viton gasket material (fluorelastomer) was irradiated at 6×10^3 Gy/h (6×10^5 rad/h), the material became progressively harder as it degraded, eventually becoming embrittled. In contrast, when samples of the same Viton material were irradiated at 100 Gy/h (10^5 rad/h), the material became progressively softer, weaker, and more easily stretched as it degraded (73).

Dose-rate effects have been studied by many different material property measurements, including gel fraction, molecular weight, volume resistivity, elongation at break, impact strength, bend strength, tensile strength, oxygen uptake, and others. The dose-rate effects can range from very large to insignificant, and this is strongly influenced by polymer type and specific formulation. In the case of dose-rate effects caused strictly by oxygen diffusion, the effect appears only over the dose-rate range at which significant changes in the extent of oxidative penetration occur. At dose rates ranging below that at which homogeneous oxidation occurs, no further dose-rate effect occurs. Similarly, at dose rates above that at which oxidation is limited to essentially a "skin effect," little or no effect may be observed. Apparently the explanation behind the erroneous assertion, which appears in a number of early papers on radiation effects on polymers (93), that dose rate is not an important factor when polymers are irradiated in the presence of air, was due to the very high dose-rate range in the studies.

Dose-rate effects can also be due to the time-dependent nature of certain steps in the degradation reaction mechanism. For two experiments, in which a material is irradiated in air to the same total dose but at different dose rates, the lower dose-rate experiment necessarily takes longer. Thus, in the lower dose-rate experiment, time-dependent steps, such as thermally induced peroxide decomposition that initiates further material oxidation (eqs. 13-15), occur to a much greater extent. This can lead to more extensive degradation per equivalent dose at the lower dose rate. Unlike dose-rate effects caused by oxygen diffusion, this type of dose-rate effect cannot be expected to disappear at dose rates below some particular value and may, in fact, become increasingly important in going to successively lower dose rates. Dose-rate effects may be due to one or more of the possible mechanisms and have been observed to occur over a wide range of dose rates. Figure 14 provides examples of dose-rate dependency; Figure 14a shows tensile elongation for a PVC cable jacketing material (94), and Figure 14b shows tensile strength for nylon strands (95).

Postirradiation Effects. Degradation of irradiated materials often continues, in storage or in use, long after the material has been removed from the radiation environment (96,97). This effect is due to continuing free-radical-mediated oxidation. This induced degradation can be very large in certain materials; it is not observed in comparable samples that had not been exposed to radiation. The postirradiation reaction is initiated by reactive intermediates formed in the course of the irradiation. It frequently involves migration of long-lived radicals from crystalline regions to amorphous regions where they can subsequently react (98), or thermal decomposition of peroxides that initiates new radical chains (94,99,100). Significant postirradiation oxidation effects may take place over weeks or years, and may result in degradation that is much more

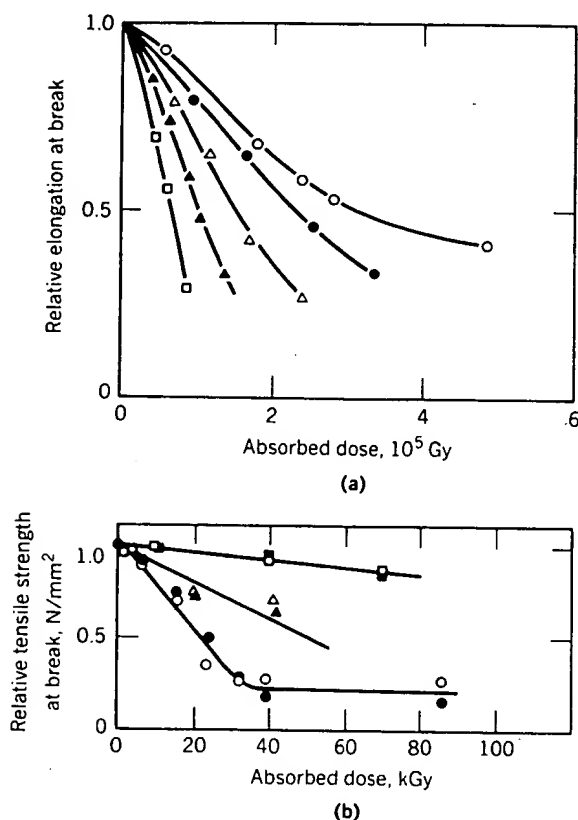


Fig. 14. (a) Ultimate tensile elongation of PVC cable jacketing γ -irradiated at 60°C at various dose rates (94); $1\text{ Gy} = 100\text{ rad}$. \circ , $9.4 \times 10^3\text{ Gy/h}$; \bullet , $3.6 \times 10^3\text{ Gy/h}$; Δ , $7.1 \times 10^2\text{ Gy/h}$; \blacktriangle , $1.7 \times 10^2\text{ Gy/h}$; \square , $3.5 \times 10^1\text{ Gy/h}$. (b) Tensile strength (relative) of nylon wires with a diameter of 0.4 mm as a function of γ -irradiation in air with different dose rates ($1\text{ Gy} = 100\text{ rad}$) (95). \square, Δ, \circ , type A; $\blacksquare, \blacktriangle, \bullet$, type B; \square, \blacksquare , 2000 Gy/h ; Δ, \blacktriangle , 43.5 Gy/h ; \circ, \bullet , 4.45 Gy/h .

extensive than that which was the immediate effect of the irradiation. Post-irradiation effects may be a major problem in certain applications. For instance, the mechanical properties of polypropylene products such as syringes, sterilized by irradiation (typically with $2.5 \times 10^4\text{ Gy}$ or $2.5 \times 10^6\text{ rad}$) initially change very little. However, after storage for six months or more, these materials may become embrittled (38,101,102). For processes in which materials are cured or cross-linked by irradiation, postirradiation effects may also create problems. The occurrence and magnitude of postirradiation effects are strongly material dependent. Materials free of crystalline regions or that are effectively stabilized against oxidation are much less prone to postirradiation effects.

Temperature Effects. In the presence of oxygen, temperature influences radiation degradation. Strong temperature effects can arise caused by changes in the rate of key processes that affect the oxidation, such as peroxide decomposition, radical migration, oxygen diffusion, diffusive loss of stabilizer additives, and others. In some cases, a striking temperature dependence may be observed,

which has been viewed as an environmental synergism between radiation and temperature. For instance, the ultimate elongation of a PVC material held in an environment of ionizing radiation (44 Gy/h or 4400 rad/h) at room temperature, decreased about 20% after 100 days. No measurable change occurred in unirradiated PVC samples kept at 80°C for 100 days. However, when samples were irradiated (44 Gy/h or 4400 rad/h) at 80°C, elongation decreased 75% after 100 days (94). Temperatures during and after irradiation are both important.

Stabilizers for Radiation-oxidative Degradation. The resistance of most polymers to radiation oxidation is significantly improved by stabilizers. The stabilization effect can be larger than that achieved in inert-atmosphere irradiation. Stabilizers are usually antioxidants, particularly radical scavengers, that interrupt the radical-mediated oxidation chain reaction (eqs. 11 and 12). Antioxidants (qv) inhibit oxidative degradation that takes place during and after irradiation. The effectiveness of antioxidants is understandable, since they inhibit radiation degradation in the absence of oxygen, and also inhibit material oxidation initiated by elevated temperature, uv light, mechanical stress, and attack by chemical agents.

A wide variety of antioxidant types have been found to exert an influence on radiation oxidation, including many commercially available compounds (29). The hindered phenols and amines are among the most effective and most widely used. Table 2 shows the stabilization of high density polyethylene by a variety of additives. The data show the dose required to reduce the elongation to half the initial value for unirradiated material; increases in radiation resistance up to a factor of six were realized with some stabilizers (103). Similar large improvements in stability have been obtained with other polymer and stabilizer types. For instance, the yield of chain scission in vulcanized natural rubber under radiation-oxidation conditions was reduced two- to threefold by incorporation of a variety of amine, quinoline, and quinone compounds at a concentration of 5

Table 2. Dose Required to Reduce Tensile Elongation to Half the Initial Value, for Polyethylene Containing Stabilizers^a

Stabilizer, 0.25%	Dose, 10 ³ Gy ^b
none	6
2-mercaptobenzimidazole	6
trilauryl phosphite	6
ionox 330 ^c	8
2-mercaptobenzothiazole	13
<i>N,N'</i> -di-(β -naphthyl- <i>p</i> -phenylenediamine) (DPPD)	15
Santonox R ^c	23
Santowhite powder, refined ^c	24
phenothiazine, Ionol ^c	
50:50	32
30:70	36

^a Ref. 103; for samples containing two stabilizers, the combined concentration equaled 0.25%.

^b 1 Gy = 100 rad.

^c A hindered phenol derivative.

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Table 3. Depolymerization Characteristics of Vinyl Polymers

Polymer	Monomer yield ^a , wt %	Volatilization/min at 350°C ^b , %	T_d , °C ^c	T_h , °C ^d	T_c , °C ^e
poly(methyl methacrylate)	92-100	5.2	330	283	220
polystyrene	42	0.24	360	364	230
poly(α -methylstyrene)	95-100	230	290	287	7
polyethylene, linear	0.03	0.004	400	415	400
polypropylene	0.2-2	0.069	380	387	300
polyisobutylene	18-32	2.4	340	348	50
polytetrafluoroethylene	97-100	2×10^{-6}	510	509	580

^a Thermal depolymerization at 300-500°C in vacuum. Refs. 5, 6.

^b Ref. 5.

^c Decomposition temperature. Ref. 4.

^d Half-life temperature at which polymer loses 50% by weight in 40-50 min. Refs. 6, 11.

^e Ref. 4.

minute (4). In general, the decomposition temperature is higher than the ceiling temperature, because the initiation of the free-radical decomposition presumably involves a dissociation of primary-valence bonds (Table 3).

Many polymers exist even at temperatures considerably above the ceiling temperature because they are in a state of metastable equilibrium. A dead polymer that has been removed from the reaction is stable and does not depolymerize unless an active end is produced by cleavage of an end group or at some point along the polymer chain. When such an active site is produced by thermal, chemical, photolytic, or other means, depolymerization follows until the monomer concentration becomes equal to $[M]$ for the particular temperature.

Many polymers actually depolymerize in a nonequilibrium manner under most conditions, and thermodynamic quantities do not allow us to predict how these polymers decompose thermally (48). It is difficult to predict the actual mode of depolymerization from thermodynamic data alone.

Energetics

For many polymers, depolymerization, characterized by the breaking of the weakest bond, is a function of the bond dissociation energy. The strength of the chemical bond corresponds to the limit of vibrational energy that a molecule may possess without bond rupture. Because vibrational energy is increased by heat, thermal stability is related to the dissociation energy of the various bonds. Thus, greater thermal stability requires bonds with greater dissociation energies.

There appears to be a proportionality between the temperature of half decomposition $T_{1/2}$ and bond dissociation energy (49).

$$T_{1/2} = 1.6 E + 140 \quad (45)$$

where $T_{1/2}$ is the Kelvin temperature at which the polymer loses half its weight when heated in vacuo for 30 min and E is the bond dissociation energy in kJ/mol (kcal/mol).